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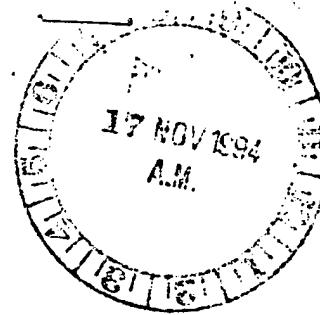
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MAJOR SOLAR PROTON EVENTS IN A 400 YEAR  
GREENLAND ICE CORE RECORD

Gisela A. M. Dreschhoff  
Edward J. Zeller

*Final*  
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# 415-YEAR GREENLAND ICE CORE RECORD OF SOLAR PROTON EVENTS DATED BY VOLCANIC ERUPTIVE EPISODES

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## A B S T R A C T

*A 122-meter firm and ice core was collected on the Greenland Ice Sheet in June, 1992, within the framework of the U. S. Greenland Ice Core Science Project 2 (GISP2). The uppermost 12 m of the least compacted portion of the core was immediately sampled and analyzed in the field; the remainder was analyzed in the National Ice Core Laboratory in Colorado. We here report on the retrieval, sampling, and analytical methods and provided complete profiles of nitrate concentration and liquid electrical conductivity from the 1992 surface through the year 1577 at a depth of 122 meters. The data series includes a total of more than 7776 individual samples that have been analyzed simultaneously for both nitrate concentration and electrical conductivity.*

*Numerous prominent anomalies occur in both the nitrate and the electrical conductivity records. The conductivity sequence contains signals from a number of known volcanic eruptions and provides an especially effective dating system at specific locations along the core. An especially distinctive signature that appears simultaneously in both the nitrate and conductivity records marks the eruptions of volcanoes on Iceland.*

*Dating is also facilitated by the rough one-year seasonal signal which appears very prominently in the nitrate record when sampling is performed at the micro-resolution (1.5 cm) sampling frequency that we used throughout the length of this core. Simple counting of the nitrate year cycles, plus the control points introduced into the record by the volcanic signal, makes it possible to resolve most events, through the 415-year period, at  $\pm$  6 months. The consistent seasonal nitrate signal includes a superimposed solar-charged particle signal, which permits delineation of a signal of solar activity well beyond that from previously known geophysical records. For example, we have been able to identify a major nitrate anomaly in the 1859-1860 period which is related to a solar flare that was optically observed in England by Carrington in 1859.*

*Our measurements extend through the Dalton (1833 to 1798) and Maunder (1715 to 1645) Minima, periods of known low solar activity. The total record obtained includes about 70 years below 1645.*

## INTRODUCTION

There has been much discussion of the use of ice cores for providing information about past climatic and environmental conditions in the polar regions. The scientific glaciological and glacio-chemical literature is providing the factual basis for these discussions. It has been generally assumed that since the great ice sheets of the polar regions are formed from snow precipitated from the polar atmosphere they must retain a signature of the conditions in the atmosphere that existed at the time of snow deposition. It is generally accepted that, in those portions of the interior of major ice sheets above the summer melt boundary, any snow that falls is retained until glacial flow mechanisms transport it away or major climatic changes cause the ice sheet to melt with the consequent loss of the retained record. For this reason, ice cores from the interiors of ice sheets are widely accepted as valid, long-term, repositories of both physical and chemical records of events from the past (Dansgaard et al., 1985; Lorius et al., 1985; Hammer et al., 1985; Mayewski et al., 1993).

Our interests have been directed toward the delineation of a solar signal in polar firm and ice sequences by measurement of nitrate concentration variations. We used techniques of applied glaciology to evaluate the variations in solar activity as it is known from historical records (Zeller and Parker, 1981). Our efforts have been concentrated on comparisons between solar activity data on individual energetic particle events and the nitrate concentration signal that could be obtained from high-resolution ice core analysis (Dreschhoff and Zeller, 1990).

However, the objective was always to extend the record back in time beyond the period of solar observation. The time period covered by this study bridges the gap between the most recent observations with satellites, radio wave absorption studies, cosmic ray counters, and geomagnetic monitors to times before the invention of the telescope. To furnish convincing evidence that a reliable record could be recovered from ice cores it was essential to conduct a long-term test. Furthermore, we

concluded that only a highly detailed ice core sampling sequence with the capability of providing information on periods ranging from a week to about one month would be required.

Charged, energetic particles incident upon the earth's polar atmosphere cause ionization of nitrogen and oxygen, generating oxides of nitrogen with nitrate ion  $\text{NO}_3^-$  as the terminal oxidation product (Swider and Narcisi, 1975). Changes in solar activity can lead to large variations in the abundance of nitrogen oxides in the thermosphere and mesosphere, particularly by auroral particle precipitation (Garcia et al., 1984). Further downward transport of these ionization products to the stratosphere is possible during the polar night. However, significant ionization within the stratosphere is essential if the nitrate signal is to be recognizable as an individual event in the snow sequence in polar ice sheets. Solar proton events can be described as a kind of catastrophic event in which a sudden outburst of solar energetic charged particles transit from the sun to the earth. Because the charged particles move along magnetic field lines that are nearly vertical above the magnetic poles, they have almost free access to the atmosphere of the auroral zone and the polar cap region.

IMP8 (Interplanetary Monitoring Platform) satellite data in conjunction with polar radio wave absorption have shown that ionization takes place even at altitudes down to as little as 20 km for the high energy component of solar protons (Armstrong et al., 1989). These results are substantiated by balloon measurements at 26 km altitude (Holzworth et al., 1987). Relatively large vertical current density enhancements in the polar stratosphere can be quantitatively interpreted in terms of atmospheric conductivity variations produced by solar proton ionization of the air. More recent data point to similar results by coupling extraterrestrial-geomagnetic events with variations in the vertical electric field at the South Pole (Byrne et al., 1991). The fallout of the chemical reaction products from the ionization may occur through

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cloud physics processes and the formation of stratospheric  $\text{HNO}_3$  (nitric acid). Temperatures can be low enough to permit nitric acid to be removed from the gas phase in air masses within the isolation of the winter polar atmosphere, especially at times when the polar vortex is active. Polar stratospheric clouds of nitric acid trihydrate (NAT) have been observed as

part of research relating to size of the cloud particles and their removal from the polar atmosphere during the polar night and early spring. Denitrification of the stratosphere, with or without dehydration, constitutes gravitational nitrate fallout or sedimentation to the polar ice sheets (Salawitch et al., 1989; Fahey et al., 1990).

### EXPERIMENTAL PROCEDURES

#### Core Drilling, Sampling, and Data Acquisition

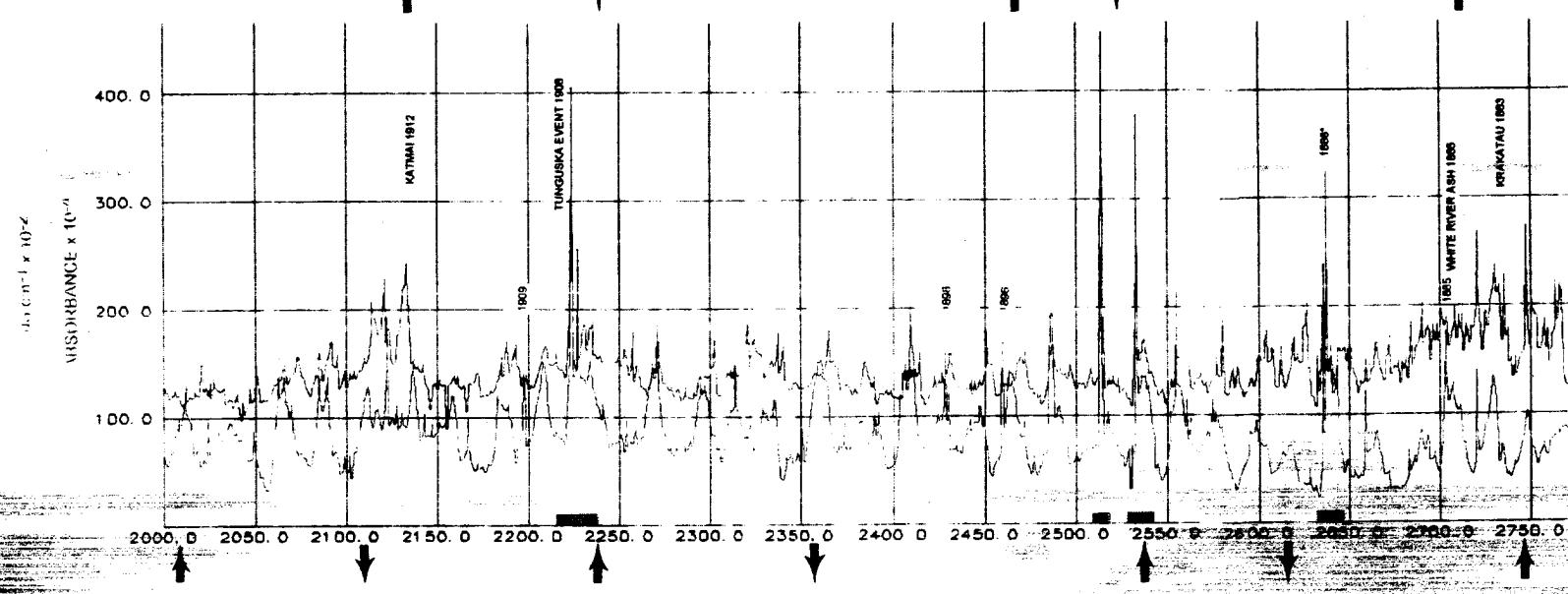
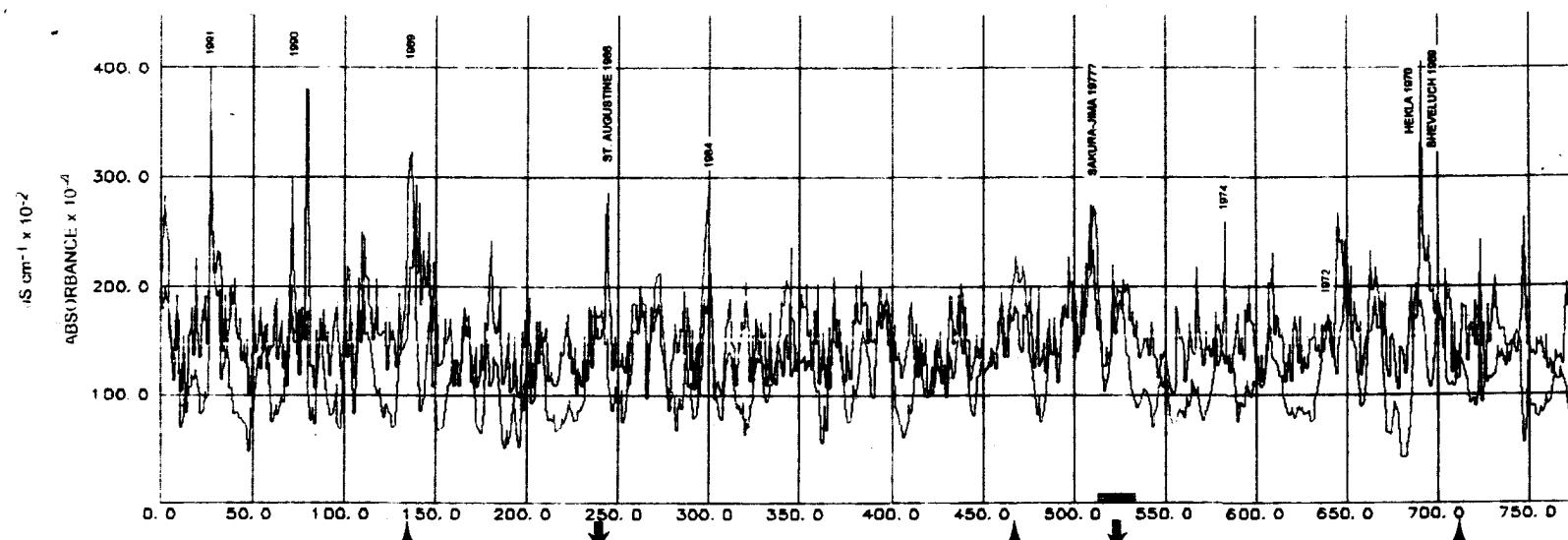
We tested very high resolution analysis techniques in Antarctica during the past six years, but only on relatively short firm cores that could be obtained by hand coring equipment. To obtain a deeper core for a longer time series, we selected an area for our test drilling that had adequate snow fall (over 50 cm per year) and temperatures well below freezing throughout the year. Such a locality was found near the center of the Greenland Ice Sheet adjacent to the GISP2 (Summit) drill site at an altitude of roughly 3,230 m, where core drilling was in progress to penetrate the entire thickness of the ice sheet. We had the good fortune to be allowed to make use of the logistic facilities connected with the operation of the GISP2 drill site and were able to use equipment capable of shallow drilling (less than 200 m) at a site less than one kilometer from the main base. Most importantly, we were assigned laboratory space where we could begin analyses of the uppermost portion of the core that is only partially compacted and is still not well suited to extensive handling and transport. We were also provided with air transportation for that portion of the core that we were unable to analyze on-site so that it could be returned to the U. S. National Ice Core Laboratory.

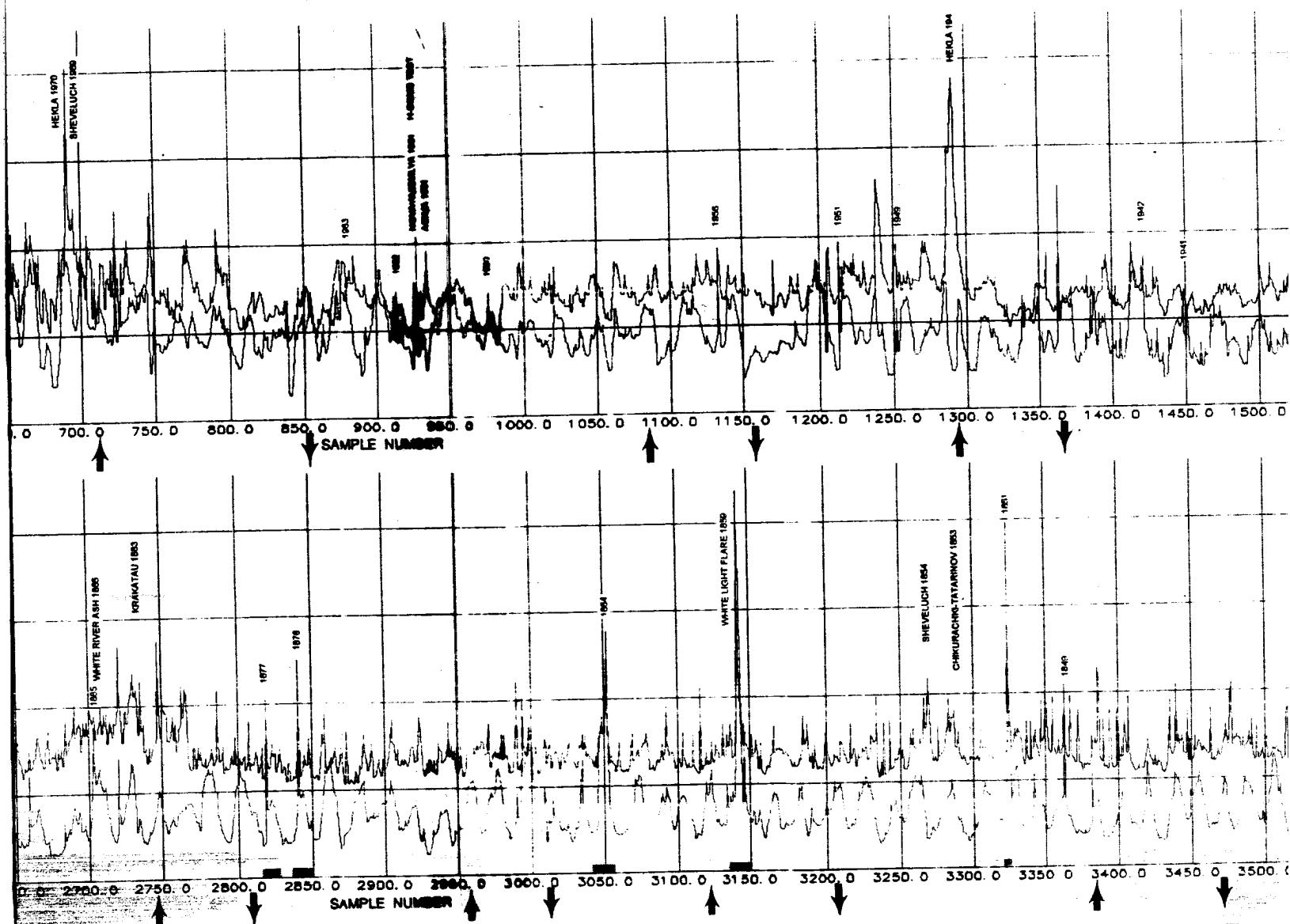
The 4-inch-diameter core (GISP2 H-core) was drilled in June, 1992, with a mechanical drill operated by the staff of the Polar Ice Coring Office (PICO). Core sections were supplied to us at the drill site where we wrapped and labeled each segment and packed them into core tubes for on-site analysis or transportation to the

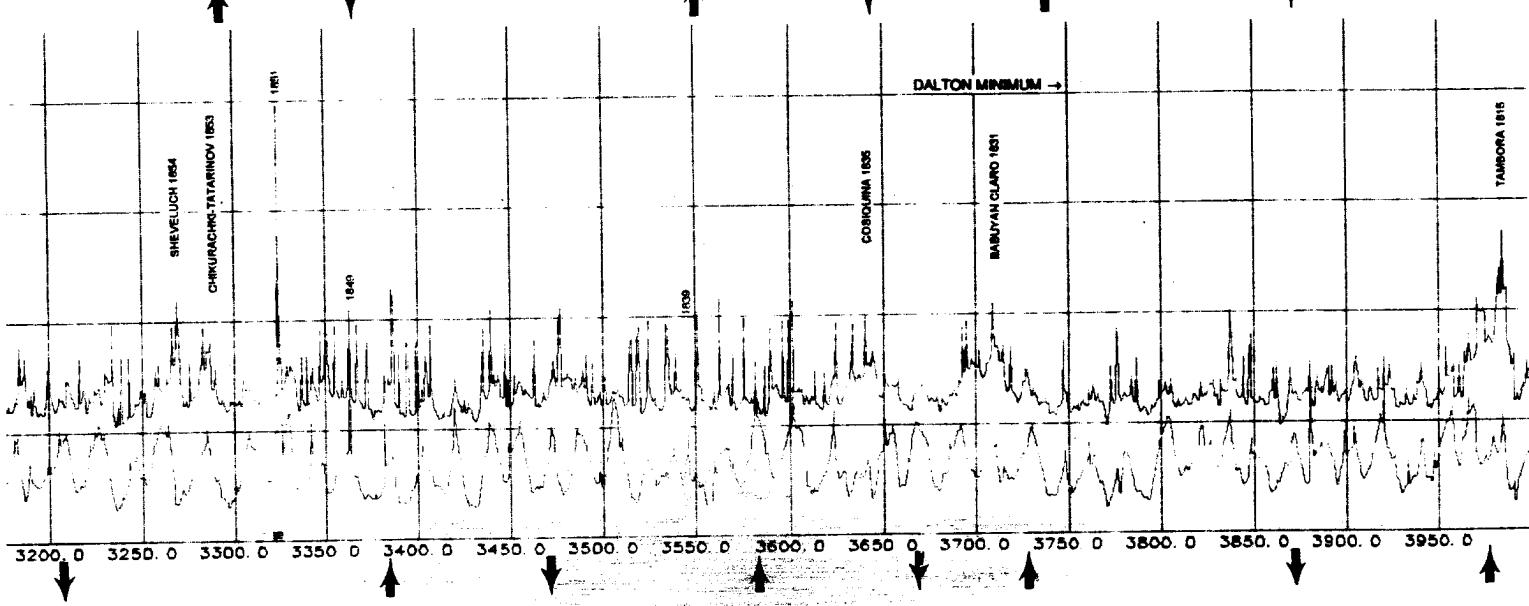
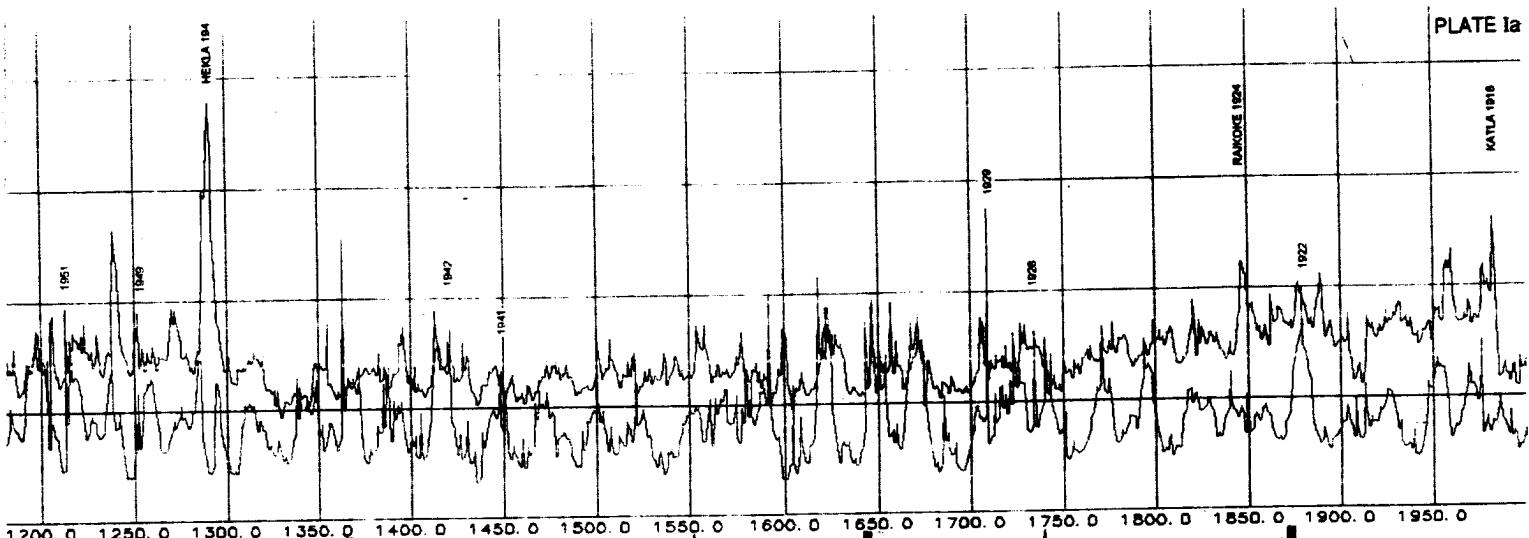
National Ice Core Laboratory (NICL) located at the Denver Federal Center in Denver, Colorado. Storage facilities for ice cores at this laboratory are held at  $-35^{\circ}\text{ C}$ .

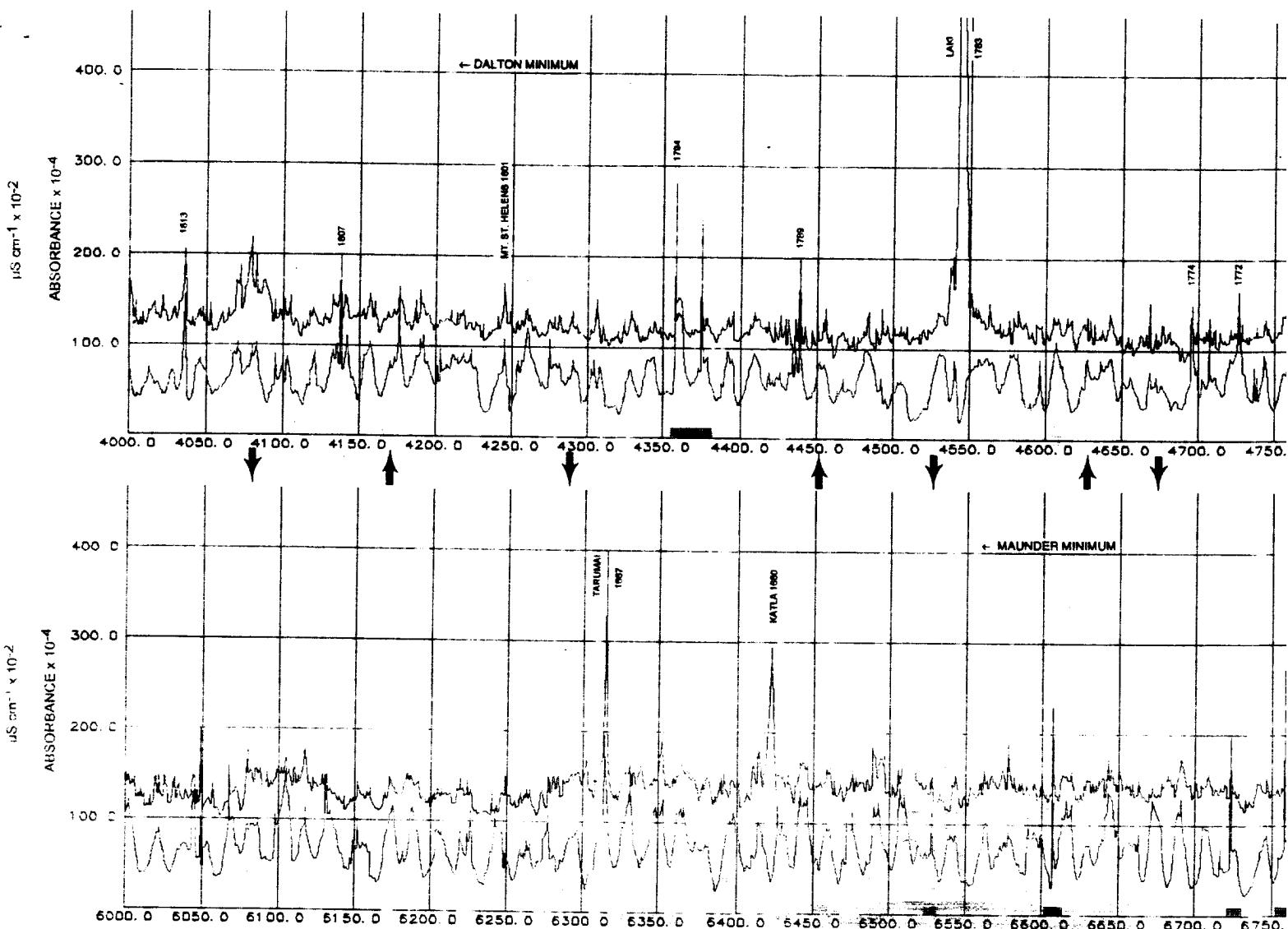
The upper 12 m of the core were sampled directly at the drill site and analyzed on-site in Greenland. All of the remaining core was subsequently sampled at NICL, in a class 100 clean room held at  $-24^{\circ}\text{ C}$ . All operations in the clean room were performed in compliance with the clothing regulations, footware, and glove-cover requirements that are appropriate to this facility. All samples were cut from the interior of the core under ultra clean conditions, using only pre-cleaned stainless steel implements as reported previously (Dreschhoff and Zeller, 1990). Each core was scraped twice and then trimmed to remove at least the outer 1.5 cm of surface material. This was done in order to remove any possible contamination of the core surfaces that might have resulted from the drilling process or have been introduced by packing, handling or shipping. After trimming and scraping off all loose ice crystals from the exposed surfaces of the core, each sample was collected by hand by sawing 1.5-cm-thick horizontal segments from the core with a stainless steel saw. Each of these samples was individually inserted into a single, pre-cleaned glass vial, sealed, and kept frozen until about one hour before actual analyses of the liquid samples.

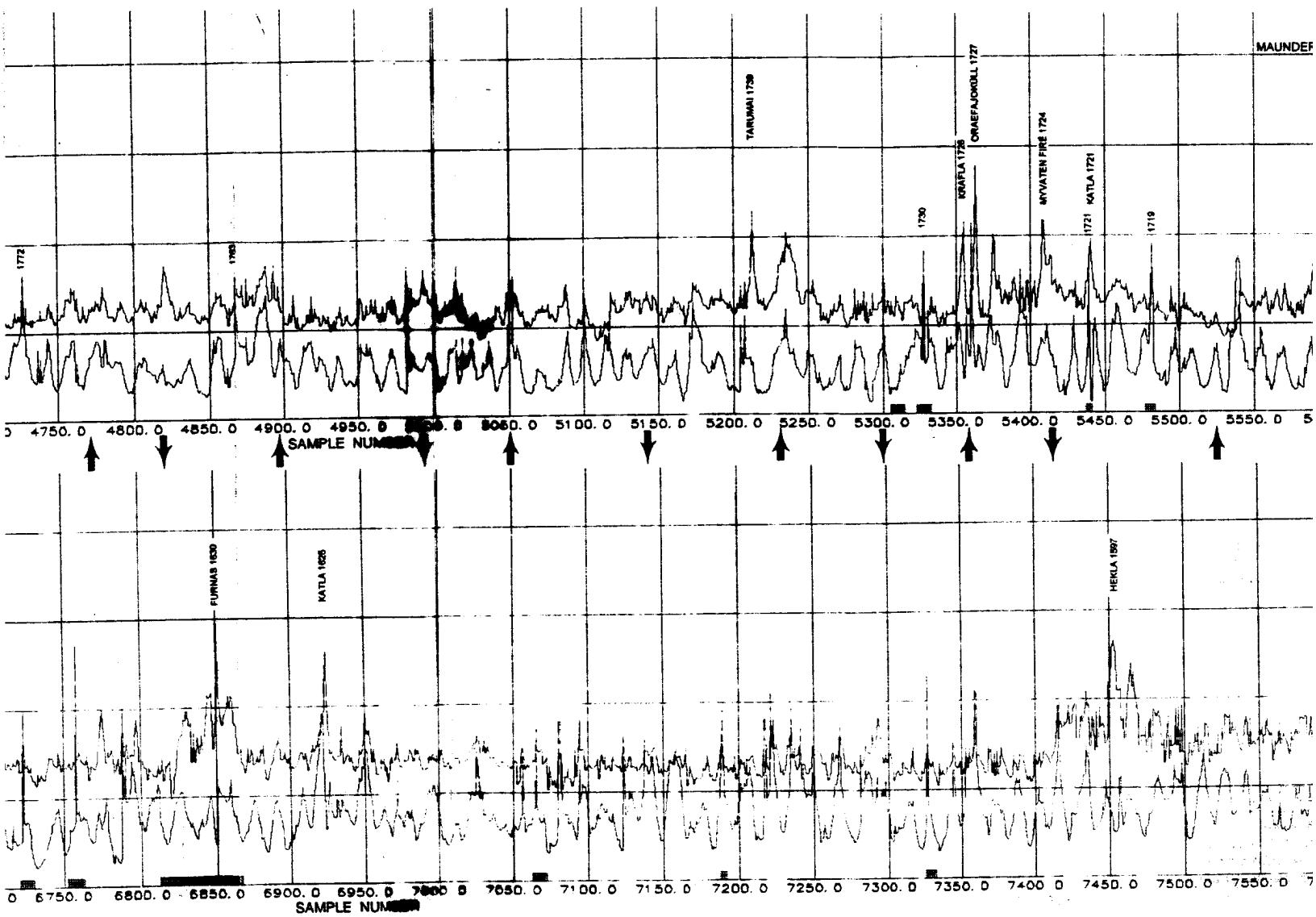
Samples were removed from the cold room and allowed to melt in the vial under room temperature conditions. Then, using a syringe with a 2.5 ml capacity, each sample was injected by hand through a stainless steel frit filter, into

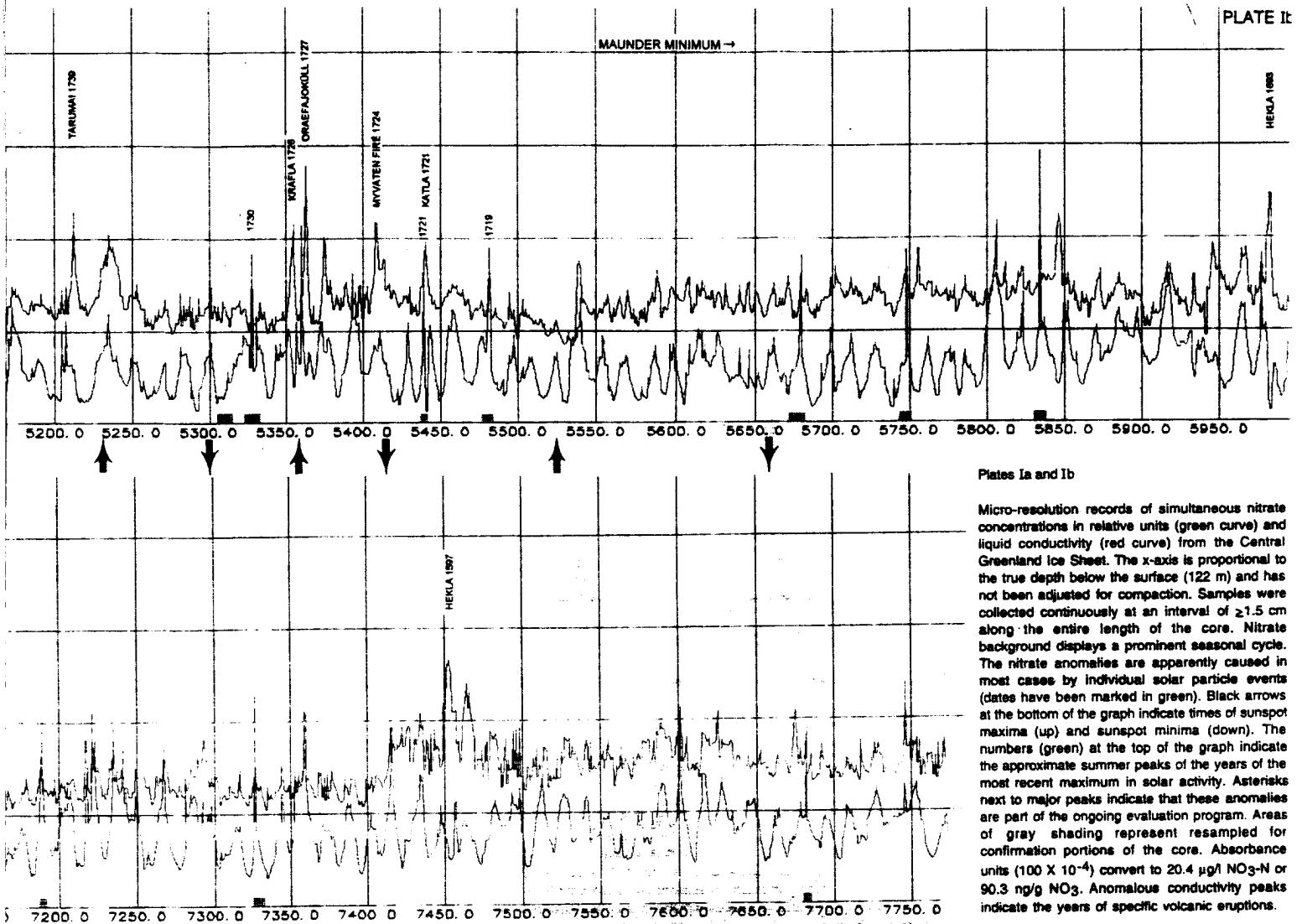












### Plates Ia and Ib

Micro-resolution records of simultaneous nitrate concentrations in relative units (green curve) and liquid conductivity (red curve) from the Central Greenland Ice Sheet. The x-axis is proportional to the true depth below the surface (122 m) and has not been adjusted for compaction. Samples were collected continuously at an interval of  $\pm 1.5$  cm along the entire length of the core. Nitrate background displays a prominent seasonal cycle. The nitrate anomalies are apparently caused in most cases by individual solar particle events (dates have been marked in green). Black arrows at the bottom of the graph indicate times of sunspot maxima (up) and sunspot minima (down). The numbers (green) at the top of the graph indicate the approximate summer peaks of the years of the most recent maximum in solar activity. Asterisks next to major peaks indicate that these anomalies are part of the ongoing evaluation program. Areas of gray shading represent resampled for confirmation portions of the core. Absorbance units ( $100 \times 10^{-4}$ ) convert to  $20.4 \mu\text{g/l } \text{NO}_3\text{-N}$  or  $90.3 \text{ ng/g } \text{NO}_3$ . Anomalous conductivity peaks indicate the years of specific volcanic eruptions.

a UV absorption cell (Beckman Model 160, selectable wavelength UV spectrophotometer) for nitrate concentration analysis (Dreschhoff and Zeller, 1990). The liquid discharged from the UV absorption cell was then directed into a microconductivity cell (Orion Model 160, conductivity meter) (Dreschhoff and Zeller, 1991). This procedure permitted the essentially simultaneous determination of both measurements. Nitrate values, in absorbance units (analytical precision  $\leq 2\%$ ) and conductivity in micro Siemens/cm ( $\mu\text{S}/\text{cm}$ ), were recorded in a notebook for entry into a computer that was running a digital signal processing program (DADiSP/32, DSP Development). After passing through the microconductivity cell, a portion of each sample was collected and has been retained in a sealed glass vial for determination of hydrogen/deuterium ratios at the Space Technology Center in Lawrence, Kansas. More than 7000 samples are currently awaiting this analysis and will be used to finalize the dating of the nitrate sequence, particularly in the upper section.

It is important to recognize that all sampling and analysis was performed using our standard method as described in this paper. Although we tested a core melting system, and we include a brief report of this test, the results of the test were not used in compiling the nitrate sequence. For this reason, none of the variability shown in this ice core record can be attributed to changes in sampling or analytical methods.

Furthermore, large portions of core remain unused and will be made available to other investigators. Whereas the standard method leaves more than 50% of the original core, the melter method leaves about 90% for further studies.

The total data record will be provided to the World Data Center A for Glaciology/Atmospheric Snow and Ice Data Center located in Boulder, Colorado. Computer disks containing this data will become freely available and can be obtained from that office.

## ANALYTICAL RESULTS

Much of our interpretation depends on a signal which we are able to acquire as a result of our micro-resolution approach. We define major or primary peaks as  $\geq 2$  standard deviations above the mean ( $\geq 2\sigma$ ), and intermediate or secondary peaks in the range less than 2 standard deviations above the mean ( $< 2\sigma$ ). The method of micro-resolution and simultaneous measurement of two trace components was developed at the Windless Bight site in Antarctica (Dreschhoff and Zeller, 1990; 1991). We drilled two shallow cores at Windless Bight, Antarctica with a separation of about 1 meter. The results demonstrated that even small individual peaks could be repeated in great detail. The precision of our methods and measurements is illustrated in Figure 1 and shows that nitrate concentrations and liquid conductivity vary only slightly between these two closely spaced cores.

This type of study was extended to two cores drilled within the same area subject to similar

meteorological conditions but approximately 10 km apart, and we found very similar results for two depth profiles (Dreschhoff and Zeller, 1991). Although not all of the details of the complete sequences repeat perfectly, we interpret this to be caused by small meteorological differences between the two drill sites. However, the major, anomalous peaks found in the first sequence also were present in the second sequence.

This same approach to verification has also been taken at the Greenland site. A total of 30 nitrate anomalies have been resampled and analyzed. With the exception of only two single-point anomalies, all others could be verified. All resampled segments are marked by shaded bars in Plates Ia and Ib. Examples of this type of reproducibility are shown in Figure 2. It shows that the major resampled peaks vary between 1.9% and 14.7% in amplitude. The plots also show the mean nitrate concentrations for 7776 data points (horizontal

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bar) and the variance of  $\pm 1$  standard deviation (vertical bar). From the purely statistical point of view, all peaks are highly significant and deviate from the mean by 8 to 4 standard deviations.

This type of high-resolution information is suppressed when viewing the complete nitrate sequence in Figure 3a, which has been subjected to a 15 point moving average. However,

the trend of background variations is very well shown. The recent upward trend beginning in about 1950 (approximate sample # 1250) may actually contain an anthropogenic component (Clausen and Langway, 1989; Mayewski et al., 1993). The electrical conductivity shows a much smaller upward trend in the upper section of the sequence, as seen in Figure 3b.

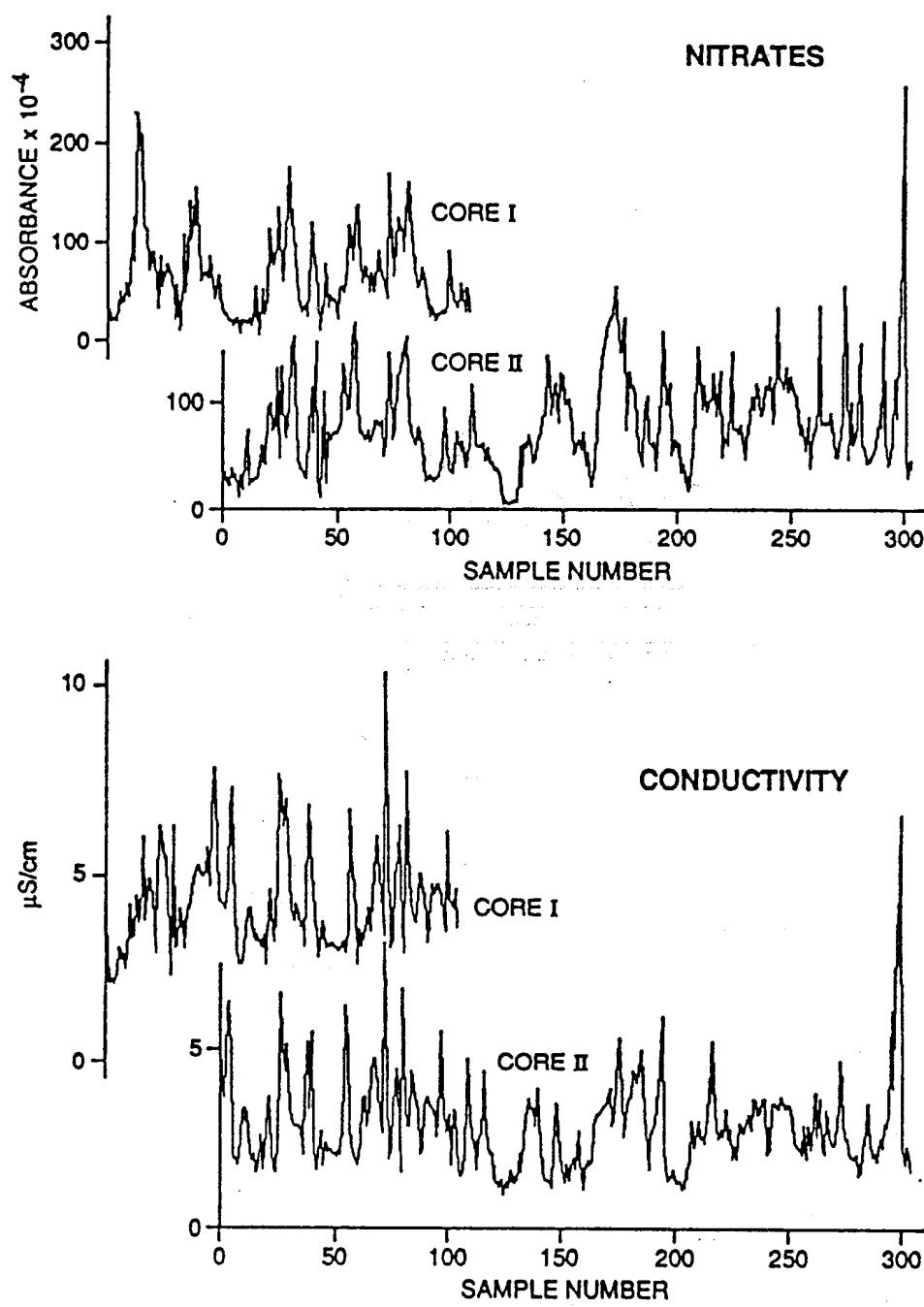
### DESCRIPTION OF THE NITRATE AND ELECTRICAL CONDUCTIVITY DEPTH PROFILES

In past field seasons we have consistently analyzed ice cores at the highest resolution that we could obtain and always with contiguous sequences so that no gaps were left unanalyzed. To illustrate the usefulness of the microresolution analytical records from the GISP2 H-ice core, we chose to plot each data point in sequence. The nitrate record has been plotted in green and superimposed upon the liquid electrical conductivity curve in red (see Plates Ia and Ib). The abscissa indicates the sample number running sequentially from 1 at the surface to 7776 at a depth of 122 m. The date of the uppermost sample is June, 1992; and the date of the year the bottom is 1577. The ordinate (numbered from 0 to 400) represents nitrate concentrations in absorbance units  $\times 10^{-4}$  and electrical conductivity in  $\mu\text{S}/\text{cm} \times 10^{-2}$ . The relative units used for nitrate analyses can be converted to concentrations in as nitrate-nitrogen ( $100 \times 10^{-4}$  abs. units =  $20.4 \mu\text{g}/\text{l}$   $\text{NO}_3^- - \text{N}$ ) or as nitrate ( $100 \times 10^{-4}$  abs. units =  $90.3 \text{ ng/g}$   $\text{NO}_3^-$ ).

The main feature in the nitrate concentration record is the prominent yearly cycle. The conductivity curve is a measure of various anions and cations present in the snow which includes a signal from volcanic activity and other marine and continental sources. The seasonality of both types of data has been known to glaciologists for many years (Mayewski et al., 1987; Taylor et al., 1992; Steffensen, 1988) in which spring/summer values tend to be higher than fall/winter values. In some cases in the nitrate record, the summer high periods show

ragged tops that often include two small spikes. This phenomenon may continue for many years so that it seems unlikely that it can be ascribable to random fluctuations. Examples are to be found between samples #6350 and #6625. We know that summer is a time of full solar illumination through the entire 24-hour period and, at the latitude of Central Greenland, this condition persists for nearly three months. It is also the time of highest temperatures. These conditions lead to an increase in sublimation (Stearns, 1992, personal communication) with the attendant increase in nitrate ion in the snow surface. It appears likely that the small nitrate concentration spikes are most probably related to the sublimation process, especially at times of reduced cloud cover or higher than normal surface winds.

Results from our conductivity profile of the liquid samples are much like those from continuous direct current electrical conductivity measurements (ECM) on the solid core (Taylor et al., 1992). The two types of sequences show very good agreement (Dreschhoff and Zeller, 1992). Although electrical conductivity can be useful to delineate years, the most effective dating is obtained from the signal caused by major volcanic eruptions. Such signal anomalies serve as time markers in the conductivity profile and are, in large part, thought to result from scavenging of stratospheric sulfates by precipitation (Delmas et al., 1982; Legrand, 1987).



**Figure 1.** Nitrate concentrations in relative units and liquid electrical conductivity records from two cores that overlap about 2 m. They were drilled about 1 m apart at Windless Bight, Ross Ice Shelf, Antarctica. These profiles show the results of our sampling and analysis method.

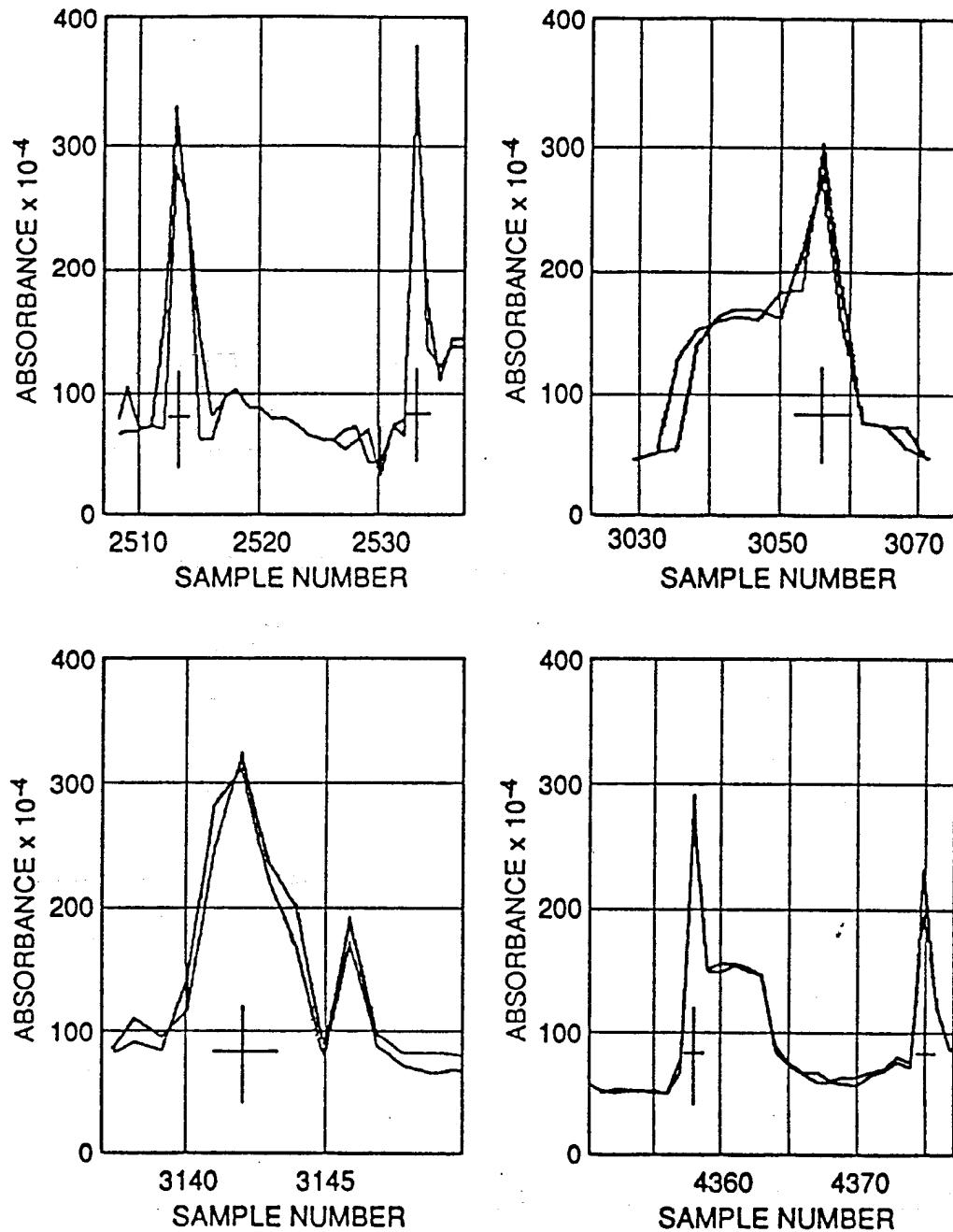


Figure 2. Examples of repeat sampling of the GISP2 H-core to test nitrate anomalies. This shows the level of reproducibility of the nitrate signal. The mean nitrate concentrations (horizontal bar) and  $\pm 1$  standard deviation (vertical bar) are indicated on each graph.

Anomalous conductivity peaks are known to be related to specific volcanic eruptions. In Plates Ia and Ib the conductivity record shows anomalies together with the times of eruptions and the names of the volcanoes that produced them. Most of the volcanic eruptions listed on Plates Ia and Ib are from Bardarson (1973), Newhall and Self (1982), Simkin and Siebert, (1993), and De Angelis and Legrand, (1994).

Plates Ia and Ib include assignments of years to some of the nitrate peaks that are of interest to this discussion. The dating is based on a combination of known volcanic events and the seasonal nitrate signal. At this time some date assignments are considered to be preliminary, but they will be finalized with completion of the hydrogen/deuterium ratio measurements.

### **The Icelandic Volcano Signature**

Because our analytical technique performs simultaneous analyses on both components of each individual sample, it is easy to recognize the Icelandic volcano signature in the ice core sequence. These opposed, dual anomalies in conductivity and nitrate furnish conspicuous time reference levels in our sequence. The combined conductivity/nitrate signal permits us to distinguish between nearby eruptions at high latitude and those that occur much farther away. Icelandic volcanic eruptions release most of their products into the upper troposphere, whereas signals from middle to low latitude volcanoes result from powerful ejections into the stratosphere with subsequent transport by planetary winds to Greenland.

Eruptions that occur geographically close to the drill site, such as those from Iceland, tend to produce large and very distinctive conductivity signals accompanied by very sharp reductions in nitrate concentrations. In fact, these anomalous decreases constitute some of the lowest nitrate values encountered in the entire record. Furthermore, there is a rapid recovery of the nitrate concentration signal to its previous or slightly higher levels of the pre-eruption values.

Two excellent examples of this are the Hekla 1947 and Laki 1783 eruptions. The number of samples from the peak conductivity value to the nitrate recovery (7 samples from Hekla and 4 samples from Laki) permits us to estimate the recovery time of 2.5 months in both cases. This type of  $\text{NO}_3^-$  reduction has also been described by Laj et al., (1993). In their investigation of changes in atmospheric  $\text{NO}_3^-$  chemistry following large volcanic eruptions, they report two sequential processes. First, the eruption results in less  $\text{HNO}_3$  being produced due to reduced partial pressure of  $\text{OH}^-$  which is used for oxidation of volcanic  $\text{SO}_2$ . Second, following the eruption, the winter values of  $\text{HNO}_3$  are enhanced via  $\text{HNO}_3$  gas phase removal by condensation on volcanic  $\text{H}_2\text{SO}_4$  aerosol surfaces and inclusion in snow grains that fall out to the surface.

Here we add a suggestion, which might also produce the effect of a sudden, short-term reduction of the nitrate signal and is based on reactions in and near the eruptive gas cloud (Burgstahler, 1993, personal communication). If some of the volcanic gases contain  $\text{H}_2\text{S}$  it can serve as a highly reactive agent (Mellor, 1930). "Although purified nitric acid does not act on  $\text{H}_2\text{S}$ , if there is only a small trace of nitrogen peroxide present (as is the case in air), the sulfide is completely decomposed forming  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4(\text{SO}_4)_2$  and nitric oxide  $\text{NO}$ ".

Hydrogen sulfide has been reported to be a constituent in volcanic gases, for example at Hekla, Iceland.

The Icelandic emission plumes, and even the giant eruption of Laki in 1783, do not usually reach into the stratosphere (De Angelis and Legrand, 1994). Therefore, eruptive cloud travel time from some of the Icelandic volcanoes to the deposition site on the snow surface of the ice sheet has been estimated to be from two to six days (Laj et al., 1993), whereas products of volcanic eruptions that are closer to the equatorial region may require as much as one year travel time. One example is that of Tambora which erupted in 1815 and its signal is recorded in snow layers deposited in 1816 (Hammer et al., 1980). Long range transport is involved and therefore the eruption must be

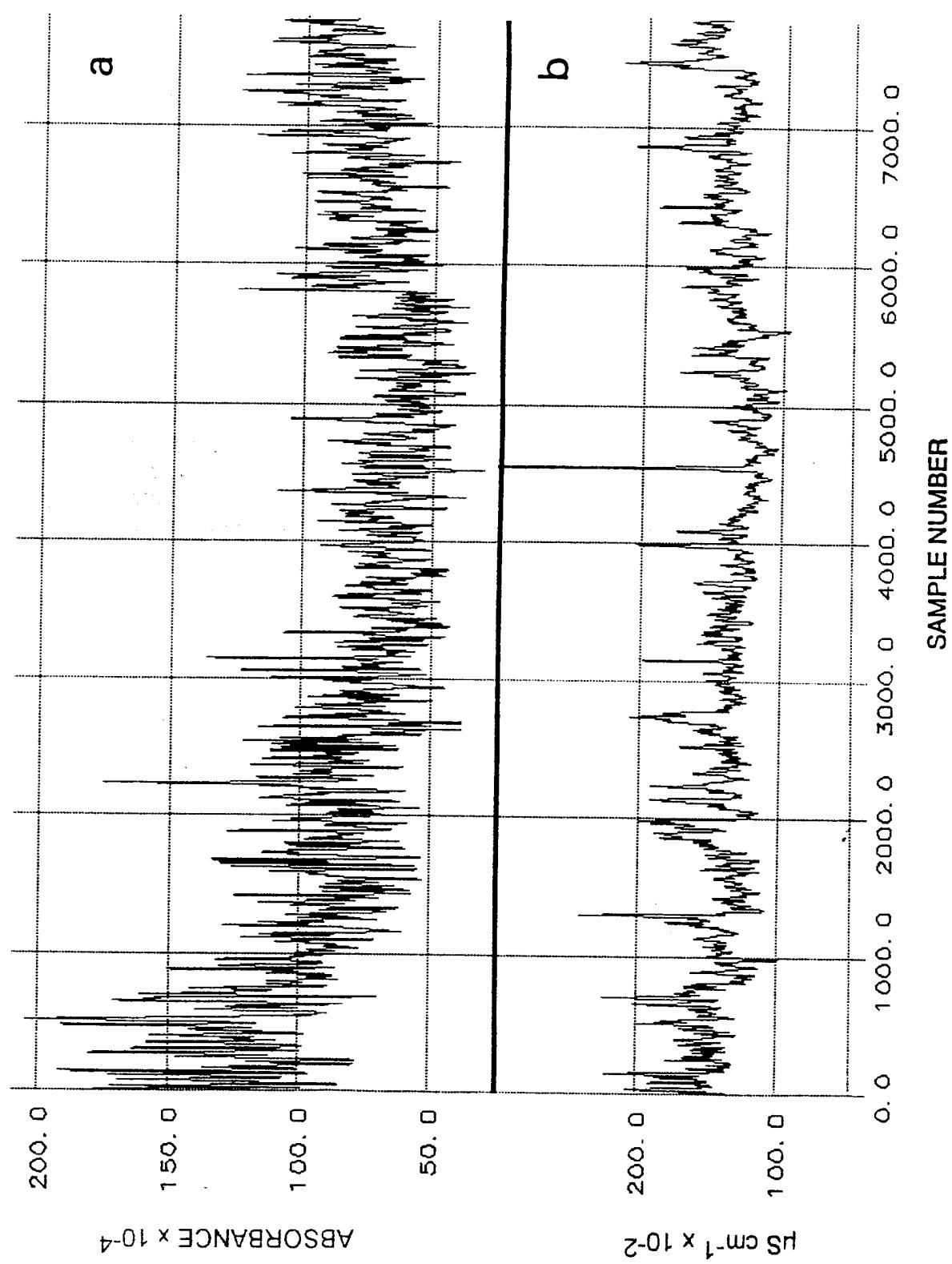


Figure 3. Complete sequence of the GISP2 H-core plotted as 15-point moving averages (Nitrate, green; conductivity, red) for the entire length of the core.

so powerful that the eruption cloud was injected into the stratosphere. If we consider the lowest yearly nitrate values for one or two years in the record adjacent to the volcanic input, they are elevated by at least 40% over directly preceding values which has also been observed by Laj et al., (1993). This type of enhancement can take place without the low temperatures of the winter polar atmosphere (Webster et al., 1994). Another very similar case is the eruption of Krakatau 1883, also resulting in a rise of the lowest background level of nitrate during and after the eruption period.

### **Major Nitrate Anomalies**

One of our objectives is to examine those anomalous nitrate peaks that are inherently significant because their peak heights are several standard deviations above the mean. Many of these peaks were verified by resampling and reanalysis (see Figure 2 and Plates Ia and Ib). On the basis of our micro-resolution sampling and analysis, we have previously suggested that these large nitrate peaks are stratospheric pulse-like contributions superimposed on the background contribution from all other sources (Dreschhoff and Zeller, 1990).

Occasionally, the large nitrate anomalies in our data are accompanied by a comparable and sharply defined positive anomaly in the conductivity signal, which is not connected with a known volcanic eruption. Nevertheless, both signals can be seen together and totally simultaneously. Since the conductivity is thought to be due in large part to sulfate originating in the stratosphere, as is nitrate also (Maupetit and Delmas, (1992), sulfuric acid aerosols could have served as surfaces where heterogeneous reactions of nitrogenous species could take place (Brasseur et al., 1990). This would result in the combined removal of both chemical species, nitrate and sulfate, by fallout and deposition of them on the snow surface. This process of heterogeneous reactions has been shown to take place by field measurements in the stratosphere after the Pinatubo eruption even without the presence of polar stratospheric clouds (Hofmann and Oltmans, 1993).

From our observations, we can conclude, that a sudden burst of sulfate load to the stratosphere does not alone tend to produce spike-like depositional features in the snow sequence following an eruption. Although some sharp nitrate peaks seem to be associated with the 1873 eruption of Krakatau, nitrate anomalies  $> 2\sigma$  are not present. The Tarumai 1667 eruption presents an exception and the simultaneous nitrate anomaly reaches  $\sim 3\sigma$ . In contrast, the  $\sim 6\sigma$  nitrate anomaly in 1859 cannot be related to a known powerful eruption. In cases where sharp, anomalous peaks occur in both conductivity and nitrates, it appears more likely that they result from primary production of  $\text{NO}_3^-$ , e.g. there has to be an enhanced supply of nitrate in the stratosphere, which subsequently undergoes condensation on sulfate aerosols.

It is necessary to ask if there is a physical process that could serve as the trigger for a spike-like burst of  $\text{NO}_3^-$  or both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  settling out of the stratosphere to the surface of the ice sheet. As discussed, polar stratospheric clouds are expected to contribute to a sharply defined stratospheric signal in the snow. Polar stratospheric clouds require the combined physical conditions of very low temperatures and sufficient amounts of condensing species (Fahey, 1991). As described earlier, the formation of nitric acid trihydrate (NAT) will take place and the NAT will tend to form a coating on ice particles in the winter polar stratosphere. There is a suggestion (Tolbert and Middlebrook, 1990) that with NAT saturation, even larger particles can form an additional coating of nitric acid monohydrate (NAM). Such particles would be able to survive higher temperatures than the NAT particles and may add significantly to the development of some of our large nitrate anomalies.

One can postulate a situation in which spike-like additions of reactive nitrogen trace species can be supplied to the stratosphere by energetic solar particles. This could occur because solar particle radiation has the ability to produce ionization deep within the polar atmosphere. In addition, lowering of stratospheric temperatures have also been observed in Antarctica where measurements have been conducted over

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the period of 1957 to 1990. The occasional cooling by several degrees Celsius is particularly apparent in high fluence solar events (Kodama et al., 1992). Enhancements of the stratospheric signal could occur due to rapid descent of mesospheric air into the stratospheric polar vortex (Fisher et al., 1993; Reeves et al.,

1994). The air packets would be able to carry downward any of the ionization products residing in the D-region or lower E-region of the polar ionosphere. This should be expected to result in evidence of nitrate production in the polar atmosphere nearest to locations where the auroral zone is directly overhead.

### THE SIGNAL OF SOLAR CHARGED PARTICLES IN THE NITRATE RECORD

An auroral zone footprint by nitrate in Antarctic snow has been reported previously (Zeller and Parker, 1981; Qin et al., 1992). These conclusions were all based on the assumption that relatively large amounts of NO<sub>x</sub> could be produced by ionization in the upper and middle polar atmosphere. Ionization leading to increases in the production of nitric oxide in the mesosphere and thermosphere of up to a factor of 8 between solar maximum and minimum have been measured by the polar orbiting satellite SME, Solar Mesospheric Explorer (Rees and Fuller-Rowell, 1989; Barth, 1990). Similar results were obtained more recently with ground based measurements (Clancy et al., 1994). Some bursts of electron (e<sup>-</sup>)-precipitation in the polar regions are also known and seem to be directly coupled to magnetospheric/ionospheric disturbances due to electrical storms in the troposphere. The frequency of these may be modulated by variations in solar activity (Markson, 1983; Inan, 1991; Frazer-Smith, 1993; Rodriguez et al., 1992).

Model calculations of the production of secondary ionization by precipitating electron bursts, indicate that in some cases, the formation of a new layer of ionization can occur at 50-70 km altitude. Such new layers may exist for up to 10<sup>3</sup> seconds following e<sup>-</sup> - precipitation bursts (Glukov et al., 1992). Such a layer may have been detected during ongoing research including radar investigations (40 to 120 km) at the New Zealand Antarctic Station (Scott Base). There is an ionization layer at 50 km altitude for which there is evidence after 16 years of data collection, that it is caused by relativistic e<sup>-</sup> fluxes, which typically last for one hour (von Biel, 1992).

Our nitrate signal analysis is in progress on two fronts.

- 1) Through the use of harmonic analysis, an attempt will be made to look for embedded signals ( $> 1 \sigma$  and  $< 2 \sigma$ ) of solar activity in what we term the nitrate background signal.
- 2) Discrete individual signals ( $\gg 2 \sigma$ ) are being examined in detail to determine whether they can be related to discrete solar proton events.

Previously, we concluded that the polar nitrate anomalies we identified in Antarctic snow sequences were most likely the result of high fluence solar proton events (Shea et al., 1993). This was based on a study involving the period of ground based instrumentation, where it was found that major solar proton events can be differentiated on the basis of the energy spectra of the particles that cause them. Two distinctly different populations of accelerated particles permit a differentiation into major peak flux and fluence events. Large peak flux solar proton events have the highest energies and frequently result in ground level events (GLEs). They probably originate near the western limb of the visible solar disk for the most efficient path along the interplanetary field line to the earth. On the other hand, large solar proton fluence events originate mainly near the central meridian of the sun. Particles from this source, together with ambient interplanetary particles, are further accelerated by powerful interplanetary shocks.

The nitrate record which we are presenting in this preliminary evaluation encompasses geophysical and solar records of varying lengths. These are the most recent satellite

records combined with ground based instruments, the geomagnetic activity record, and the optical observations of the solar disk recording white light flares and, the longest record, the number of sunspots. Anomalies contained in these records have been used as a basis for marking some of the major nitrate anomalies by the years of their occurrence in Plates I and II. Particular emphasis has been placed on anomalies that occur (a) during the northern hemisphere winter period, (b) during the declining phase of the 11-year solar activity cycle. For this purpose the monthly mean sunspot numbers (Gentile, 1993, Personal communication) were most advantageous. This record extends back as far as 1750, whereas yearly mean sunspot numbers are available as far back as 1710 (Eddy, 1977). The maxima and minima of sunspot numbers throughout the historical record have been indicated by black arrows pointing upward and downward, respectively (Plates Ia and Ib).

We find the nitrate anomalies to be mainly associated with irregularities within the frequency distribution of sunspot numbers during the declining phase of the 11-year sunspot cycle. These are basically abrupt increases in solar activity, when otherwise the activity has been relatively weak, associated with quiet conditions in the heliosphere. In our nitrate anomalies, major solar outbursts during the declining phase of the solar cycle occur with high statistical significance. We are currently attempting to make a more detailed examination using the 400-year sequence that we have obtained.

Nitrate peaks at sunspot maxima have not been marked in Plates I and II because they are part of the ongoing work of identification and interpretation. However, an increased occurrence of major nitrate anomalies at or near sunspot maximum preceding the period before about 1920 is of particular interest. This period apparently represents a time when less "chaotic" conditions existed in the heliosphere (Sargent, 1979). These conditions are best seen by examining records of the 27-day Bartles rotation-geomagnetic Recurrence Index. The general trend of the Recurrence Index exhibits

lowest values during a solar maximum followed by an increase in values during the declining phase of solar activity and reaching maximum values during solar activity minima. Sargent, (1979) observed, that before about 1920, the 11-year response of the Recurrence Index is less distinct. This seems to be mainly due to higher recurrence values at or near solar maximum. For this reason, conditions could be maximized for an individual discrete event to cause reactions in the earth's polar atmosphere and ultimately be detected as a nitrate anomaly.

The most spectacular example is to be found in the giant optical solar flare observed in September, 1859, by Carrington (Frazier, 1982). This was a very rare white light flare of extraordinary power and brilliance, which could be observed even without special optical filters. This flare apparently occurred at longitude west 12° on the solar disk as seen from the earth. This advantageous position permitted a high flux of extremely energetic solar protons to reach the earth very rapidly (Shea, 1993, personal communication). A geomagnetic storm was registered on earth only 17 hours after the observation was made. An unusual auroral display was also observed as far south as the tropics at the time of this geomagnetic storm.

#### **The Dalton and Maunder Minima**

During the historical period when sunspot numbers have been recorded, two extended periods of reduced solar activity have occurred, the Maunder Minimum from 1645 to 1715 (Eddy, 1976) and the Dalton Minimum from 1798 to 1833 (Feynman and Silverman, 1980). Associated with both of these periods we find a reduction in frequency of the anomalous nitrate peaks. Following the Dalton Minimum (approximate sample numbers 4300 to 3700) we record the first very large nitrate anomaly (dated 1851, 8 sigma). This peak seems to be associated with renewed solar activity during the declining phase of solar cycle 9 in conventional numbering. There seems to be little question of the reality of a prolonged minimum in solar activity as recorded by the number of sunspots, the Maunder Minimum (approx.

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sample numbers 5550-6650). This period has been reexamined by Eddy (1983) and by Silverman, (1993). This 70-year period of low solar activity or very weak solar wind, would have resulted in increases of galactic cosmic rays (GCRs) entering the heliosphere. Evidence of significant increases of radionuclide production by GCRs comes from two independent methods.  $^{14}\text{C}$  content in tree rings provides such a record of solar variability (Damon et al., 1978), and  $^{10}\text{Be}$  in ice cores (Beer et al., 1990). From this type of work it is also known that galactic cosmic rays also display the 11-year solar modulation.

The question has been raised whether the sun continued to modulate galactic cosmic rays even during the Maunder Minimum (Jokipii, 1991). There are indications from high resolution  $^{14}\text{C}$  data, that the variation in the intensity of GCRs is clearly dominated by a period longer than 11-years (Kocharov, 1988). This has been interpreted as probably resulting from the continuation of solar magnetic field reversals that affect the drift component of the GCR modulation in the heliosphere. If this process were in operation, it would result in an  $\sim$  22-year periodicity in the data (Jokipii, 1991).

This hypothesis may be supported by experimental results. Basically three different periods of short duration show reduced  $^{14}\text{C}$  production in very high-resolution  $^{14}\text{C}$  tree ring data. The average increase in  $^{14}\text{C}$  production during the Maunder Minimum is interrupted temporarily in three different periods, occurring at  $\sim$  1660,  $\sim$  1675 and 1700. In the latter case, nitrate anomalies of up to 6 sigma above the mean are associated with the time around 1700 (sample number 5836). The other two previous periods are much less clearly defined in our nitrate profile. Beginning with a 3 sigma anomaly in 1647 ( $\sim$  sample number 6600 in our nitrate record) the next comparable anomaly occurs at 1667 (sample number 6317) and another period about 20 years later centered at approximate sample number 6100. The first half of the Maunder Minimum seems to be dominated by two long periods of about 20 years each. The emergence from the Maunder Minimum into the clearly  $\sim$  11 year cyclicity is

indicated in the  $^{14}\text{C}$  record (Kocharov, 1988) by minima in 1720 and 1728. Both periods are coincident with nitrate anomalies of  $\sim$  3 sigma and  $\sim$  4 sigma, respectively. These discussions are of a preliminary nature and no direct correlations have been established. Future work and data evaluation will be required to test these observations.

### The Nitrate Background During the Maunder Minimum

Although the Maunder Minimum is a clearly defined feature in the South Pole record (Zeller and Parker, 1981), there are a number of reasons we should not necessarily expect the background nitrate signal to reflect greatly reduced levels of concentration in the Greenland ice sheet. The geographic South Pole is located directly within what we term the auroral footprint (Qin et al., 1992). In contrast, the central Greenland ice sheet does not have the same spatial location, partly because of the only 9 degree offset between the geographic and geomagnetic coordinates in the northern hemisphere as compared to the 15 degree offset in the southern hemisphere. Therefore, South Pole Station would be more directly influenced by the auroral ionization source of nitrates. Also, the two polar regions are very different geographically.

The high central ice sheet of Greenland seems to reflect the climatic conditions that occur in the coastal region (see Barlow and White, 1992). This is in sharp contrast to the interior of the Antarctic continent. There the warmest, wettest, particle-laden air arrives with the relatively infrequent winds blowing from the quadrant of the Weddell Sea and the Ronne Ice Shelf. These conditions are rare and occur on the order of about 10 days per year, mainly in the summer (Hogan et al., 1982). Throughout much of the year, and particularly during darkness, the most frequent direction from which surface air arrives at the South Pole is from the interior of East Antarctica. Furthermore, most precipitation at the altitudes of 3000 m on the Antarctic ice sheet falls from clear skies (Bromwich, 1988).

In contrast to the high Antarctic polar plateau, the Central Greenland ice sheet may be influenced by varying large-scale meteorological conditions, including changes in storm tracks, as well as source regions for the atmospheric trace constituents (Charles et al., 1994;

Mayewski et al., 1994). It is clear that the arctic atmospheric nitrate reservoir was not depleted during the Maunder Minimum and we find that the seasonal nitrate background signal was not significantly reduced during that period.

## DISCUSSION AND CONCLUSIONS

Our approach has been to distinguish between nitrate background in ice and a clearly defined signal that appears to originate in the stratosphere. These anomalies seem to be most often associated with years in the declining phase of the solar cycle. This interpretation is clearly substantiated by the 400-year micro-resolution record of nitrate concentrations. These peaks have been marked in Plates Ia and Ib by the years of their occurrence in the dated sequence. Some nitrate anomalies that occur at or near maxima of solar activity are also designated in Plates Ia and Ib. This is represented by the very large and apparently very energetic event of 1859.

Smaller but nevertheless very distinct peaks in the Greenland sequence have also been identified in Antarctica (Shea et al., 1993). We see two events, one in 1928 and one in 1909. The 1909 event was apparently associated with a major geomagnetic disturbance at the end of September of that year. In 1928, the major geomagnetic disturbance of July is probably associated with the anomaly in Antarctica, whereas in Greenland it is more likely that the white light flare of September causes the anomaly in the ice sequence (Shea, 1990, personal communication).

By associating the polar nitrate anomalies with individual solar proton events, we may be able to study solar processes encompassing several centuries. Based on solar initiated disturbances of the polar stratosphere and ionosphere, we conclude that these anomalous nitrate peaks constitute a signature of the state of the polar stratosphere following a "catastrophic" event such as the major solar flare of September 1859. A quantitative evaluation of such ionization events should be a very

important goal. However, this requires the development of calibration sources that can be tested by evaluating their effect on the complex interaction between ionization, production, and fallout of nitrate to the ice sheet and various other atmospheric parameters that are site dependent. In fact, one such calibration standard may exist in the form of a kind of "standard candle" which constitutes the 60-megaton hydrogen bomb test fired on Novaya Zemlya on 30, October, 1961. This nuclear explosion was the largest atmospheric test in history and occurred at a very high latitude. We believe that the signal from this explosion can be pinpointed in our nitrate profile (sample #928) (see Plate Ia and Figure 4).

At sample #935, the concentration peak in the conductivity curve indicates the eruption of Askja volcano in central Iceland on October 26, 1961. The sharp decline in nitrate level is shown by the green nitrate curve and this is another example of the classic Icelandic volcano signature that is so prominently displayed in our micro-resolution time series. Shortly after reaching the low in nitrate a rapid rebound begins. This is followed by a double spike in nitrate which reaches a concentration anomaly of 3 sigma. The sharp high is followed by a low which is, in turn followed by a second spike about 2/3 the intensity of the first anomaly. We think it likely that the first and most intense spike represents the primary nitrate fallout reaching Greenland after completing a transit around the north polar basin from Novaya Zemlya. It seems likely that the second, weaker spike arises from further fallout from a second circuit around the north polar basin. We intend to examine the record further to attempt to see if it is possible to use the 60-megaton blast to calibrate other ionization events.

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Another conspicuous example is the anomaly near sample #2225 in Plate I. At this location in the profile we observe an anomalous peak which is quite large. A nitrate anomaly ( $\sim 5$  sigma) is almost immediately followed by another nitrate anomaly ( $< 9$  sigma) which is accompanied by a conductivity anomaly as well. At this time we interpret this to be due to the Tunguska event, the meteorite air burst over Siberia, 30 June, 1908 (Peel, 1993; De Angelis and Legrand, 1994). There is no certainty about this event, but it has been estimated that an explosion of a stony asteroid occurred at 10 km altitude, releasing 10-20 megatons of energy (Chyba et al., 1993). During such an explosive event it should not be surprising that major atmospheric ionization would take place and would leave a record in the high-resolution nitrate sequence in Greenland.

Since we have stated repeatedly that unambiguous detection of short-term pulses of nitrate enhancements directly related to solar proton events (SPEs) seem to depend primarily on the presence of the polar winter vortex, we must be concerned about its stability during the winter period and into early spring. We know from the work of Labitzke and van Loon, (1989), that during the period of January and February, 1956 the arctic vortex was weakened in response to the QBO being in a westerly phase. For this reason, we might expect the February 1956 SPE signal (sample number 1130) to be reduced in snow that fell in this period of time. Furthermore, during the westerly phase of the QBO, the winter hemisphere of the earth can be supplied by a much larger aerosol reservoir extending to the equator, whereas the planetary waves are shielded from the equator during the easterly phase (Trepte et al., 1993).

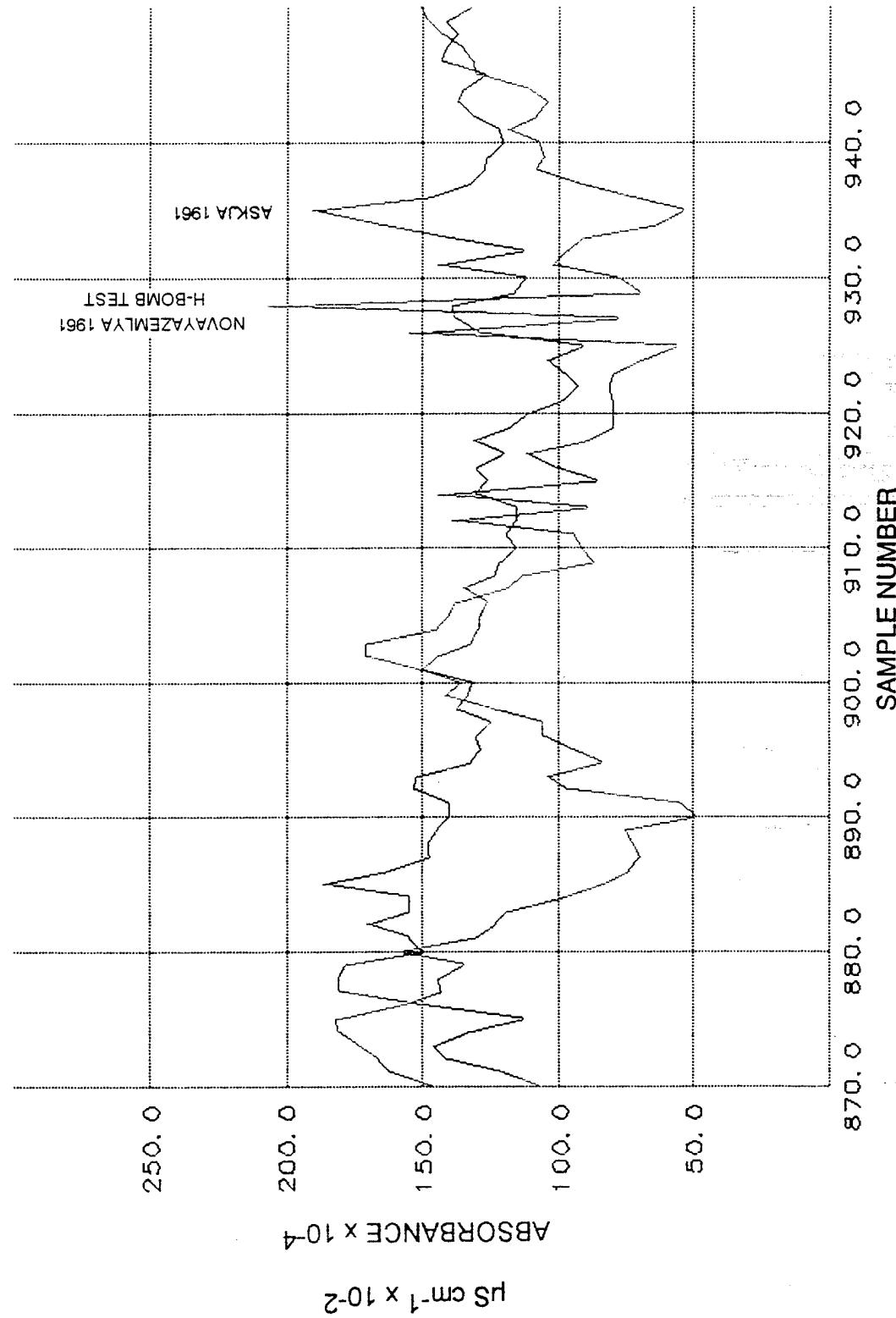
From this discussion, it is clear that we are dealing with a very complex relationship among solar-terrestrial interactions on the one hand and polar atmospheric dynamics and chemical reactions on the other. In this context, we call attention to the uppermost part of our record labeled 1992-1989. This period corresponds to the recent maximum in solar activity, solar cycle 22. We intend to evaluate this time period very carefully in conjunction with additional

micro-resolution dating of the sequence because this was a period characterized by a large number of unusual solar proton events (Shea and Smart, 1993).

$^{10}\text{Be}$  measurements with about one-year resolution in ice cores have clearly shown that the 11-year periodicity and longer term features like the Maunder Minimum are visible in the data (Beer et al., 1990). It is always important to consider the effects of polar meteorology on signals of solar activity and cosmic ray flux in ice sequences (Lal, 1987). However, we consider it highly unlikely that the correlations that we observe between historical solar activity variations and nitrate anomalies can be attributed to chance coincidence.

We find that the fine structured signals are retained in a medium that undergoes various stages of compaction and metamorphism. A number of processes may take place influencing the distribution of chemical traces in the upper snow layers. Some degree of metamorphism resulting from internal sublimation is known to occur and surface snow may also be viewed as a mechanical filter for the particulate content of surface air. Due to pressure differentials caused by strong winds, the air volume in the snow (30-50%) will be continuously displaced (Gjessing, 1977).

Despite such diagenetic processes taking place on or near the surface or in the snow pack, it is clearly possible to maintain recognizable original signals. By working in a specific area for many field seasons, we observed that major anomalous peaks in nitrate were maintained as a sharp signal in the micro-resolution record (a) spatially over  $\sim 10$  km and (b) with time and increased compression (Dreschhoff and Zeller, 1991). Smaller nitrate peaks were shown to be less consistent. The evidence seems to show that the higher the concentrations the less they are affected by changes after deposition. The influence of diagenetic processes (metamorphism) of the snow may be stabilized through chemically "poisoning" defect sites (LaChapell, 1963). In short, snow that is very high in chemical traces such as high  $\text{NO}_3^-$  concentrations, sometimes in association with volcanic acids and other chemical species, may retain its



**Figure 4. Short segment of the GISP2 H-core.** Each sample number represents  $\geq 1.5$  cm along the core. The nitrate anomaly at sample number 928 has been interpreted as resulting from stratospheric ionization from the largest known nuclear detonation ( $\sim 60$  megatons). Our micro-resolution records permit a temporal resolution of two high latitude events that left a signal in the Greenland snow. They were the eruption of Askja in Iceland (conductivity) on 26 Oct. 1961 and the H-bomb test on Novaya Zemlya on 30 Oct. 1961.

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signal integrity for long periods of time. The lack of direct knowledge about the structure of interfaces and the difficulty of experimentally monitoring the mechanisms and dynamics of ion transfer present fundamental questions that have not yet been answered. The work reported by Mulvaney et al., (1988) and Dibb et al., (1993) are examples of this type of study.

In future work we believe that we will be greatly aided by our new development of an automatic melter, which may yield even higher resolution and consequently better signal recognition. This melter has already been tested to the extent that it almost perfectly repeated results on nitrate concentrations that we had obtained by our standard sampling method (see sample numbers 6815 to 6870). The new apparatus permits continuous melting using a 1 inch diameter gold plated cylinder in the interior of the core. Use of this apparatus will greatly increase our sampling resolution from 1.5 cm per sample to about 5 mm per sample while leaving about 90% of the remaining core for other investigators.

In conclusion, the purpose of this report was to present the complete with a preliminary evaluation that includes descriptions of some of the difficulties generally encountered in working with snow and ice data. The main objective of the continuing research is the identification and quantification of large solar proton events and their ionizing effects on the polar atmosphere. This association of nitrate anomalies and solar proton events as described in our 400-year Greenland record must be viewed as a first order approximation of the combined effects of the conditions outside the earth's atmosphere and

within the terrestrial polar atmosphere. We recognize that the interpretation of the data that we obtain must be integrated with information about the winter polar vortex, polar stratospheric clouds and associated stratospheric denitrification. From our previous detailed work on relatively short sequences in Antarctica we know that the polar snow clearly shows a response to short-term physical inputs of energetic solar particles. Our current micro-resolution record from Greenland must await detailed analysis before firm conclusions as to the nature of all of the nitrate anomalies can be reached.

The record that we have obtained on solar proton events is certainly not complete. A record from one polar ice sheet contributes at best only about half of one year because the record is based on atmospheric dynamics and cloud physics specific to that polar region. In addition, each half year contribution is further limited by a number of factors, among which wind blowing across the snow surface probably plays the largest role. In some years, on the central Greenland ice sheet, the winter layer may even be missing (Jaffrezo et al., 1994). Nevertheless, the polar nitrate anomalies that we observe could hardly be derived from a random distribution of surface and depositional effects. We emphasize the distinct signal of volcanic events which provides an independent check of individual events in the ice record. At high latitudes, stratospheric dynamics and large inputs from solar charged particles combine to produce a recognizable signal in micro-resolution analytical sequences. Through the use of records from cores from both polar regions it appears that these implications can be tested rigorously.

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### Interactions and Activities

1. The following papers were presented or coauthored at the AGU Meeting, San Francisco, December 1993:

Major Particle Events for Solar Cycles 5 to 22 in a Micro-resolution Record of Nitrates from the Greenland Ice Sheet by G. Dreschhoff, E. J. Zeller, M. A. Shea and D. F. Smart.

A 200 Year Micro-resolution Record of Nitrate and Conductivity for the Central Greenland Ice Sheet by E. J. Zeller and G. Dreschhoff.

On the Solar Modulation of Cosmic Rays and Solar Flares During Deep Minima of Solar Activity by L. D. Martin, G. Kocharov, G. Dreschhoff and E. J. Zeller.

Temporal and Spatial Evaluation of the Solar Magnetic Field: a View from the Sidelines, by G. Kocharov, G. Dreschhoff, E. J. Zeller and L. D. Martin.

2. During July and August of this year a substantial period of time was spent at the National Ice Core Storage Laboratory at the Denver Federal Center where we completed sampling and analysis of the 120 meter ice core from Central Greenland.

3. A manuscript titled "415-year Greenland Ice Core Record of Solar Proton Events Dated by Volcanic Eruptive Episodes" has been accepted for publication by the Tertiary and Quaternary Institute of Lincoln, Nebraska at the University of Nebraska and is presently in press.

4. G. Dreschhoff has been named to the Board of Governors of the American Polar Society, September 1994.

5. A lecture titled "Nitrates in Greenald Ice, Volcanic and Solar-terrestrial Links" was presented at the Space and Plasma Physics Seminar, Department of Physics and Astronomy University of Kansas, October 1994.